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(54) **Process for the production of a colloidal boehmite**

Verfahren zur Herstellung von kolloidalen Böhmit

Procédé pour fabrication boehmite colloïdale

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(56) References cited:
EP-A- 0 015 196
EP-A- 0 304 721
US-A- 4 676 928

EP-A- 0 025 817
US-A- 4 117 105

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Description

This invention relates to a process for the production of a colloidal boehmite.

In the production of ceramic forms of alumina with a very fine crystalline size of less than one μm , it is highly desirable to use as a starting material a similarly finely divided form of the precursor material. This is particularly true when the process used is a sol-gel process such as is described in, for example US Patents 4,314,827 or 4,623,364. Such patents use a sol of alumina monohydrate which is then gelled either by reduction of water content or more usually by peptization using an acid. This gelled form may then be dried, comminuted and sintered at relatively low temperatures to give alpha alumina structures with very fine and uniform particle sizes. The above process may be carried out in the presence of modifying agents such as magnesia, zirconia, silica, titania, chromia or compounds that break down to such oxides under sintering conditions, and/or seed materials that favor the formation of the alpha alumina form. Such seed materials can be any one of those materials that are stable under the reaction conditions and which have the same crystal structure as the target alpha alumina and similar lattice parameters to those of alpha alumina. The preferred seed material is of course alpha alumina itself but other seed materials within the above definition such as alpha ferric oxide, added ab initio or generated in situ, can be used in many circumstances.

As indicated above it is highly advantageous in the operation of such a process that the boehmite dispersion be as fine as possible and as free as possible of agglomerates which tend to convert as such and produce similar agglomerates in the alpha form. It is found that such agglomerates are associated with a reduction in the properties of the final products. For example, abrasive grits made of such material are often less effective than those in which the crystal size is uniformly microcrystalline.

It is apparent therefore that there is substantial advantage in securing a feedstock that has the uniform microfine crystal structure referred to above. One method of obtaining such products is described in USP 4,117,105 in which an alumina trihydrate is first calcined to increase its surface area through a partial dehydration and then autoclaved to achieve crystallization and rehydration. The result is apparently to produce a product with a crystallite size smaller than that of the starting material.

Another process for producing a water dispersible alumina from a hydrolysate of an aluminum alkoxide is described in US Patent 4,676,928. In this process the alumina slurry is aged at a pH of 5 to 9 at a temperature above 70°C for enough time to convert the greater part to a colloidal sol.

A further process of making a boehmite product is known from EP-A-0 304 721. Said process uses a seeding mechanism to produce a boehmite from precursor material.

Other processes for the production of alumina in a sol form are described in US Patents 2,590,833; 2,787,522; 2,915,475; 3,357,791 and 3,966,893.

However none of the above methods are capable of converting an alumina monohydrate precursor having a substantial degree of particulate inhomogeneity into a product with essentially uniform, ultrafine, (ie less than 100 nm (1000 angstroms)), particles that are particularly suitable for the production of alpha alumina by a sol-gel route. The present invention provides such a process and thus makes available to the maker of high grade alpha alumina products, or the catalyst monolith producer where alpha alumina is not required, a feedstock that had previously been unacceptable on account of the presence of agglomerated particles.

This is achieved according to the present invention by a process for the production of a colloidal boehmite according to independent claim 1. Further advantageous features, aspects and details of the invention are evident from the dependent claims, the description and the examples. The claims are intended to be understood as a first non-limiting approach of defining the invention in general terms.

The invention thus refers to manufacturing dispersible boehmite, i.e. the manufacture of finely divided boehmite, (sometimes called alpha alumina monohydrate), from less finely divided boehmite and the like.

The present invention provides a process for the production of a colloidal boehmite which comprises providing a slurry of boehmite having a dispersibility, as hereinafter defined, of less than 70% and acidifying the slurry to a pH of about 3.5 or lower by adding acid in sufficient quantities to partially dissolve the boehmite and to reach the above value but insufficient to cause the boehmite to dissolve completely, then digesting the acidified mixture at a temperature of from about 150 to about 200°C under a pressure of from about 5.15 to about 20.6 kg/cm² (0.5 to about 2 MPa) for a time of from about 0.15 to about 4 hours so as to produce a colloidal boehmite with a dispersibility of at least about 90%.

The aluminous starting material can be a boehmite with a relatively high percentage of aggregated particles.

The dispersibility is defined as being the weight % of solids that cannot be centrifuged out of the dispersion by centrifuging in a polypropylene tube, (18mm x 100mm), at 3500G for 3 minutes. This property is therefore a measure of the presence of larger agglomerates in the material. The dispersibility is a guide to the quality of the final product that can be obtained from the boehmite by sintering. If a product with agglomerates is used, that is a product with a relatively low dispersibility, the final product will have a high "Spot Index". This parameter is measured by preparing abrasive grain with a size of 50 grit, (according to FEPA specifications), by the seeded sol-gel process described in US Patent 4,623,364. This grain is then mounted in an epoxy resin, and the grain surface is polished with a diamond powder. The

polished surface is examined under visible light with a microscope at a magnification of 250x. The blemishes in each grain are then counted. After 50 grains have been counted, the spot index, (SI), is calculated from the following formula:

$$SI = 2(A+2B+3C+4D)$$

where: A is the number of grains with 1-3 blemishes;
B is the number of grains with 4-6 blemishes;
C is the number of grains with 7-10 blemishes; and
D is the number of grains with 11 or more blemishes.

The Spot Index is therefore a direct indication of the number and size of agglomerates which appear in the final grain as blemishes.

An important feature of the present invention is that the thermal treatment is carried out at a pH of 3.5 or lower and preferably 3 or lower. As will be shown below, operation at higher pH values leads to poor dispersibility and a high spot index. Thus, while conversion to boehmite is efficiently achieved using the higher pH values described in prior art processes, the result is a boehmite with an excessive quantity of non-dispersible particles which are reflected in blemishes in any abrasive alpha alumina particles prepared therefrom.

The temperature at which the treatment is carried out is also significant. In general this temperature should be from about 150 to about 190°C and more preferably from about 160 to about 180°C. Since the higher temperatures tend to be more effective in reducing the Spot Index, temperatures in the upper halves of the above ranges are more preferred.

The heating is preferably conducted under autogenous pressure which conventionally reaches from about 10.3 to about 15.45 kg/cm² (1 to about 1.5 MPa). The pressure can of course be generated artificially if desired without changing the essential nature of the invention. Such pressure can range from about 5.15 to 20.6 kg/cm² (0.5 to 2 MPa) but preferably lies within the same range as autogenously generated pressure.

The time of the treatment is conveniently from about 10 to about 120 minutes. In general there is little benefit to be derived from a treatment longer than from about 30 to about 90 minutes at the treatment temperature.

The process of the invention can be carried out in the presence of other additives conferring specific advantages such as electrolytes for the control of viscosity and solids content; compounds that liberate a gas upon heating, (such as metal carbonates), if a porous end product is desired; modifiers such as magnesia, zirconia, chromia and the like; grain growth inhibitors such as silica; and drying agents.

Of particular utility is the addition of seed material. Where the material treated is boehmite with a comparatively low dispersibility, it may often be advantageous to incorporate a seed material that enhances the conversion of such boehmite to alpha alumina at lower temperatures. Such seed materials have the same crystal structure as alpha alumina with crystal lattice parameters that are close to those of alpha alumina. The best example is of course alpha alumina itself but other compounds with close lattice parameter matches, such as alpha ferric oxide or a precursor of such a compound, can be used. The seed can be added before or after the hydrothermal treatment though addition before often makes the dispersion problem more tractable.

Where the compound is a precursor of boehmite it can often be useful to incorporate a seed material that promotes the formation of boehmite in the same way that an alpha-conversion seed material promotes the formation of alpha alumina. A typical boehmite-conversion promoting material is boehmite itself.

Where a seed material is present, it is important that it be present in a well dispersed, finely divided form. Seed particle sizes below one µm are in general preferred and particles less than 0.1 µm are even more preferred.

It is also within the scope of this invention to subject the boehmite or boehmite precursor having seed material incorporated therein, to a further process in which a sol of the treated boehmite is gelled and then formed, dried and fired to convert to alpha alumina. This corresponds to the processes described for example in US Patents 4,314,364; 4,623,364; 4,744,802; 4,964,883; (Jimmies); Published PCT Applications 90/08744 and 90/02160; and the like.

The hydrothermal treatment of the invention can be carried out on a batch or a continuous basis and the water, the boehmite or the boehmite precursor can be subjected to a prior or subsequent deionisation process if so desired.

The invention is now further described with reference to the following examples which are for the purpose of illustration only and should not be interpreted as imposing any necessary limitation on the essential scope of the invention.

EXAMPLE 1

This Example illustrates the control over particle size and dispersibility by a treatment according to the invention.

Several test samples were given a hydrothermal treatment by placing 3.0g of Kaiser forming grade alumina monohydrate, (boehmite), in a large pyrex test tube along with 30ml of tap water and 1.2ml of 18 wt% of nitric acid, (enough to lower the pH of the mixture to below 3.5). The tubes were sealed by melting the end. Each tube was placed in a steel canister and placed in a preheated oven maintained at about 185°C ±5°C. The autogenous pressure is estimated at about 11.33 kg/cm² (1.1 MPa).

As controls, the starting material was evaluated without the hydrothermal treatment and also with the hydrothermal treatment except for the exclusion of the acid.

It was found that, after 3 hours of acidified hydrothermal treatment, the initial powdery slurry had turned to a translucent gel filling the available liquid volume. There was no evidence of any of the original powder remaining. As time in the autoclave increased, the appearance of the gel gradually became more opaque and after 96 hours resembled dairy cream or a talcum powder dispersion.

The results are summarized in the following Table 1.

TABLE 1

Hours in Autoclave	Acid (+/-)	Dispersibility %	Ultimate Crystallite Size (Å)**	Hardness after sintering *** (GPa)
Control				
0	-	30	64 +/- 1	<3
3	-	35	64 +/- 1	<3
0	+	30-35	64 +/- 1	<3
Evaluation				
1	+	39	75 +/- 1	ND
3	+	95	119 +/- 3	5-6
8	+	97	259 +/- 14	5-6
24	+	92	481 +/- 52	5-6
96	+	63	842 +/- 160	5-6

* 1 Angstrom = .1 nm

** Measured using an x-ray diffraction line broadening technique and the equation:

$$\frac{1.11 \times Y \times 57.3}{(B1/2 - b1/2) \cos \frac{(2\theta)}{2}}$$

where: Y = CuK radiation = .154 nm (1.54Å)

b1/2 = width in degrees at half maximum of a reference material with crystallite size >300 nm (3000Å)

B1/2 = Width in degrees at half maximum of the sample of interest

2θ = peak angle in degrees

57.3 = conversion factor radians/degrees

The 120 reflection was used in the measurement.

*** Product sintered for 1 hour at 1400-1425°C

A Wilson Tukon microhardness tester, model LR, was used

As can be seen from the above, the presence of the acid significantly increased the dispersibility of the boehmite provided the time of treatment is not too prolonged. The particle size grew at a rate consistent with classical theory, ie as a function of the cube root of time. When the particles became very large there was a tendency to agglomeration and the dispersibility decreased markedly.

EXAMPLE 2

This Example describes the results of subjecting a different alumina monohydrate to the hydrothermal treatment described in Example 1.

A sample of W.R. Grace SRA spray dried sludge SMR 14-1617 was given the hydrothermal treatment described in Example 1 for 3 hours at a temperature of 185°C except that 1.0g of magnesium nitrate were added to the mixture. Before treatment the dispersibility was 37% and afterwards it was 97%. The material, as received and before treatment, would not sinter to a dense body whereas the treated product formed a translucent gel, dried to a rigid green form and sintered well to a hardness of 15 +/- 1 GPa, (>80% of theoretical).

EXAMPLE 3

This Example shows that the process of the invention is also effective with a seeded boehmite.

An aluminum monohydrate (200g) available from Conoco under the trade name, Catapal, was mixed with 500ml of water in a waring blender for one minute. To the resulting slurry were added 11.6g of an alpha alumina slurry containing 12.9% by weight of sub-micron alpha alumina.

Nitric acid was then added to the resultant slurry with stirring, in the form of an 18 wt% solution. A 100g sample was kept as a reference and the remainder was autoclaved in a PARR one litre model 4521 stainless steel autoclave equipped with a stirrer mechanism. The heat-up time was approximately 45 minutes and the time at the designated temperature is shown in the Table 2 below. After this the autoclave was switched off and cooled to ambient temperature over a period of about an hour. Upon cooling the samples were tested and the results appear in Table 2.

TABLE 2

Temp. (°C)	pH	Ratio Acid/Boehmite	Time (h)	Dispersibility		Spot Index		Hardness (GPa)
				Before	After	Before	After	
160	2	N.D.	0.5	94.9%	98.2%	400	205	20.3
160	2	N.D.	1.0	94.9%	98.0%	400	250	20.3
160	3	0.012	0.5	61.9%	95.9%	400		20.8
160	3	0.012	1.0	61.9%	95.5%	400	349	21.1
160	4	0.005	0.5	60.8%	54.1%	400	N.D.	<10.0
160	4	0.005	1.0	60.8%	53.8%	400	N.D.	<10.0
180	2	N.D.	0.5	94.9%	N.D.	400	16	20.6
180	3	0.012	0.5	61.9%	98.2%	400	6	20.6
180	4	0.005	0.5	60.8%	47.3%	400	N.D.	<10.0

Hardness was determined after sintering the hydrothermally treated sample at 1400°C in air for 5 minutes.

As can be readily seen from the above data increasing the amount of acid increases the initial dispersibility but that at lower levels of acid, (but still at a pH below 4), the initial low dispersibility can be improved by the hydrothermal treatment of the invention. In addition it is clear that increasing the temperature results in a highly beneficial improvement in the Spot Index. Finally, operation at pH of 4 resulted in a very low hardness in the final sintered product.

EXAMPLE 4

This Example follows the procedure of Example 3 except that a different boehmite is used.

The alumina monohydrate used was Versal 450, available from Kaiser Chemical Co. and made by neutralization of sodium aluminate liquor. In addition the seeding slurry was added in an amount of 23.2g. The results appear in Table 3.

TABLE 3

Temp. (°C)	pH	Ratio Acid/Boehmite	Time (h)	Dispersibility		Spot Index		Hardness (GPa)
				Before	After	Before	After	
160	2	N.D.	0.5	44.7	71.5	>1000	N.D.	18.0
160	2	N.D.	1.0	44.7	N.D.	>1000	38	17.4
160	3	0.023	0.5	46.3	71.5	>1000	400	N.D.
160	3	0.023	1.0	46.3	78.6	>1000	400	14.2
180	2	N.D.	0.5	44.7	98.8	>1000	21	19.0
180	3	0.023	0.5	46.3	97.9	>1000	226	19.3
Control (No Autoclave)								
--	3	0.023	--	46.3	--	>1000	--	<10

As will be apparent, the hydrothermal treatment markedly improves the dispersibility and the Spot Index very dramatically. In addition the sinterability, as indicated by the hardness, improves significantly as a result of the treatment.

EXAMPLE 5

This Example duplicates the procedure of Example 4 with the difference that acetic acid replaced nitric acid. Enough of the acid was added to bring the pH to 3.3 prior to autoclaving. After autoclaving for half an hour at 160°C, the Spot Index had declined from 400 to 106, whilst at 180°C the corresponding decline was from 400 to 9.

From the above Examples it can readily be appreciated that the process provides a most advantageous route to obtaining a boehmite with a greatly improved dispersibility at a relatively low cost. Moreover this process can use relatively poorly dispersible starting materials which in general are cheaper. Because the starting material is a fluid slurry, sol or gel, dispersion of additives or seed materials in the precursor is easy. The process also offers the opportunity to control crystallite size in the final product.

Claims

1. A process for the production of a colloidal boehmite which comprises providing a starting material which is a dispersion of a boehmite,

acidifying the dispersion to a pH of 3.5 or lower by adding acid in sufficient quantity to lower the pH to the above level but insufficient to cause the boehmite to dissolve completely,

characterized by

providing the dispersion with a dispersibility of less than 70%,

subjecting the dispersion to a hydrothermal treatment by heating under a pressure of from 0.5 to 2 MPa (5.15 kg/cm² to 20.6 kg/cm²) at a temperature of from about 150 to 200°C for a time of from 0.15 to about 8 hours so as to produce a colloidal boehmite with at least 95% dispersibility.

2. The process according to claim 1 in which the starting material comprises in addition a seed material effective to promote the formation of alpha alumina.
3. The process according to one of the preceding claims in which the hydrothermal treatment is performed on a dispersion with a pH of from about 2 to 3.
4. The process according to one of the preceding claims in which the reaction is conducted under autogenous pressure.

5. The process for the production of a colloidal boehmite according to one of the preceding claims in which said pH ranges from 2 to 3 and said pressure ranges from 1.0 to 1.5 MPa (10.3 to 15.45 kg/cm²) so as to produce a colloidal boehmite with a dispersibility of at least 95% and a Spot Index reduced to less than 50% of the figure obtained using the untreated starting material.

Patentansprüche

1. Verfahren zur Herstellung eines kolloidalen Boehmits mit der Bereitstellung eines Ausgangsmaterials, wobei es sich um eine Dispersion eines Boehmits handelt,

dem Säuern der Dispersion auf einen pH-Wert von 3,5 oder weniger durch Zugabe von Säure in ausreichender Menge, um den pH-Wert auf den oben genannten Wert zu senken, jedoch nicht ausreichend, um ein vollständiges Auflösen des Boehmits herbeizuführen,

gekennzeichnet durch:

Verleihen der Dispersion einer Dispergierfähigkeit von weniger als 70 %,

Aussetzen der Dispersion einer hydrothermalen Behandlung durch Erwärmung unter einem Druck von 0,5 bis 2 MPa (5,15 kg/cm² bis 20,6 kg/cm²) bei einer Temperatur von etwa 150 bis 200°C über eine Zeitdauer von 0,15 bis etwa 8 Stunden zur Herstellung eines kolloidalen Boehmits mit einer Dispergierfähigkeit von mindestens 95 %.

2. Verfahren gemäß Anspruch 1, bei dem das Ausgangsmaterial zusätzlich ein Impfmateriale aufweist, das zur Förderung der Bildung von Alpha-Aluminiumoxid wirksam ist.

3. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem die hydrothermale Behandlung mit einer Dispersion mit einem pH-Wert von etwa 2 bis 3 erfolgt.

4. Verfahren gemäß einem der vorhergehenden Ansprüche, bei dem die Reaktion unter autogenem Druck erfolgt.

5. Verfahren zur Herstellung eines kolloidalen Boehmits gemäß einem der vorhergehenden Ansprüche, bei dem der pH-Wert zwischen 2 und 3 liegt und der Druck 1,0 bis 1,5 MPa (10,3 bis 15,45 kg/cm²) beträgt, um einen kolloidalen Boehmit mit einer Dispergierfähigkeit von mindestens 95 % und einem Fleckenindex (Spot Index), welcher auf weniger als 50 % der unter Verwendung des unbehandelten Ausgangsmaterials erhaltenen Zahl verringert wird, herzustellen.

Revendications

1. Procédé pour la production d'une boehmite colloïdale qui comprend la fourniture d'une matière de départ qui est une dispersion de boehmite,

l'acidification de la dispersion à un pH de 3,5 ou moins en ajoutant de l'acide en quantité suffisante pour abaisser le pH à la valeur indiquée ci-dessus, mais insuffisante pour provoquer la dissolution complète de la boehmite,

caractérisé en ce que

la dispersion est fournie avec une dispersibilité inférieure à 70 %,

la dispersion est soumise à un traitement hydrothermique par chauffage sous une pression comprise entre 0,5 et 2 MPa (entre 5,15 kg/cm² et 20,6 kg/cm²) à une température comprise entre environ 150 et 200°C pendant une durée comprise entre 0,15 et environ 8 heures de façon à produire une boehmite colloïdale ayant une dispersibilité d'au moins 95 %.

2. Procédé selon la revendication 1, dans lequel la matière de départ renferme en outre un matériau d'ensemencement efficace à favoriser la formation d'alpha alumine.

3. Procédé selon l'une des revendications précédentes, dans lequel le traitement hydro-thermique est mis en oeuvre sur une dispersion ayant un pH compris entre 2 et 3.

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4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la réaction est mise en oeuvre sous une pression autogène.
5. Procédé pour la production d'une boehmite colloïdale selon l'une des revendications précédentes, dans lequel ledit pH est compris entre 2 et 3 et ladite pression est comprise entre 1,0 et 1,5 MPa (entre 10,3 et 15,45 kg/cm²) de façon à produire une boehmite colloïdale ayant une dispersibilité d'au moins 95 % et un indice de tacheture réduit à moins de 50 % du chiffre obtenu en utilisant la matière de départ non traitée.

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